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Orientational Order Parameter Undecyloxy-Cyanobiphenyl (11OCB) and Dodecyloxy-Cyanobiphenyl (12OCB) by using Optical Birefringence Method

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ABSTRACT

High resolution optical birefringence studies throughout the nematic and smectic A phases of undecyloxy-cyanobiphenyl (11OCB) and dodecyloxy-cyanobiphenyl (12OCB) have been performed to evaluate orientational order parameter ($<P_2>$) as a function of temperature at wavelength λ=632.8 nm. The temperature dependence of the birefringence (Δn) data have been exploited to assess $<P_2>$ using a well-known Haller's extrapolation method. Effectively, in the nematic and smectic A phases the values of $<P_2>$ have been fitted with the estimated values from Maier-Saupe mean field theory for nematic liquid crystals and McMillan mean field theory for smectic liquid crystals. Experimentally obtained $<P_2>$ values have been compared with those achieved from Maier-Saupe mean field theory and McMillan mean field theory. The agreement between experimental and calculated $<P_2>$ values at nematic-isotropic (N-I) is much higher than experimental $<P_2>$ values.

Keywords: Haller's extrapolation method; Optical birefringence; Orientational order parameter.

1. Introduction

In condensed matter physics, liquid crystalline state of matter plays significant role for application in display devices as well as fast operating shutters, tunable photonics, nonlinear optics, broad range filters, holographic devices, etc. [1-4]. The knowledge concerning different interesting properties such as refractive indices, birefringence, viscosities, dielectric anisotropies, electric, magnetic susceptibilities and elastic constants are dreadfully necessary for the use of liquid crystals for different types of devices. Hence, in order to invent better materials for display applications most remarkable features of liquid crystals have been characterized. Despite considerable properties of applicability in display applications, order parameter can predict the nature of the liquid crystalline phase transformations.

Orientational order parameters are among the most interesting properties of liquid crystals have been extensively studied, which organize nearly all the physical properties [5-8]. Various methods have been developed to determine the temperature dependence of order parameters. Among abundant techniques, optical method has been considered as one of the best [9-12] method.

Alkyloxycyanobiphenyls are very well-known liquid crystalline compounds and these are extensively studied due to their high positive optical anisotropy and good chemical stability. They exhibit long thermal ranges of phases with the change of the number of alkoxy chains. It may be mention that in the investigated series for nOCB (n=11,12) compounds show only smectic A phase. Much work has been done on the members of this homologous series from different techniques [10-13].

In the present paper we report the comprehensive analysis of the temperature dependence of orientational order parameter for undecyloxy-cyanobiphenyl (11OCB) and dodecyloxy-cyanobiphenyl (12OCB) using birefringence data obtained from high resolution optical birefringence measurements. Haller's extrapolation method, which is

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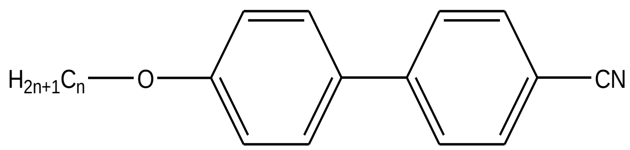
rather ambiguous, has been considered to calculate the $<P_2>$ in connection with temperature significantly from birefringence data. The evaluated $<P_2>$ values have been compared with Maier-Saupe mean field theory [14] solely for nematogenic liquid crystals and McMillan's theory [15] for smectogenic liquid crystals. Our calculated values have been compared with literature value [10-14]. It is found that our experimental $<P_2>$ values are in good agreement with theoretically obtained the same

2. Experimental

2.1. Materials

The nOCB (n=11,12) compounds were obtained from Merck, U.K. and were synthesized and purified by Prof. R. Dabrowsky at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. Its purity was higher than 99.9%, and no further purification was needed. The transition from smectic A phase to isotropic phase occurred for two compounds 11OCB and 12OCB respectively showing any other intermediate phase between them.

The general structural formula and the transition temperatures of the two compounds well-known family of cyanobiphenyls are given below:



nOCB (n=11,12)

undecyloxy-cyanobiphenyl (11OCB): Cr 71.5°C SmA 87.5°C I

Dodecyloxy-cyanobiphenyl (12OCB): Cr 70°C SmA 90°C I

2.2. Optical transmission (OT) method

The intensity of the laser beam have been employed to derive the optical birefringence ($\Delta n = n_e - n_o$) through high resolution temperature scanning technique. These laser beam have been directed to pass through a linear cell (procured from AWAT Co. Ltd., Warsaw, Poland) filled with liquid crystal. The cell have been placed between two crossed polariser in such a way that they are parallel to each other.

To investigate the phase interruption concerning with experimental set up two laser beam , one was He-Ne laser having wavelength λ=632.8 nm and the other was green laser of wavelength λ=532 nm have been managed. A heater made up of brass have been engaged for inserting the cell on it and its temperature have been monitored by means of a temperature controller (Eurotherm PID 2404) having a precesion of about ± 0.1 K. The cell temperature also maintained by this temperature controller.

The heater temperature have been altered by a rate of about 0.5 K min^{-1}, so that the interval between two successive raeding raised by 0.025 K. The transmitted optical intensity is an oscillatory function of the optical phase difference $\Delta\varphi$. The optical birefringence and the phase difference are closely connected. So to derive the temperature variation of optical birefringence we have to measure phase difference first considering light intensity assuming the following relation [16],

$$I_t = \frac{\sin^2 2\theta}{2}(1-\cos\Delta\varphi) \qquad (1)$$

where θ is the angle made by the polarizer with the optic axis and is set at 45^o to optimize the measurements.

$$\Delta\varphi = \frac{2\pi}{\lambda}\Delta nd \qquad (2)$$

where d is the sample thickness. Several cooling and heating run have been performed to acquire suitable outcome. The quite precession has been done by this method which was better than 10^{-5}.

3. Theoretical Background

3.1. Determination orientational order parameter from Haller extrapolation method

The birefringence, Δn, values have been obtained from high resolution optical transmission method is used to evaluate the order parameter $<P_2>$ in the nematic as well as in smectic phases. It is well known that any physical property of nematic liquid crystals closely connected with orientational order parameter. Hence, According to Haller approximation the order parameter can be expressed as,

$$< P2 >= \left(1 - \frac{T}{T^*}\right)^\beta \qquad (3)$$

Latter, de Gennes [2] suggested that orientational order parameter can be the measure of any anisotropic physical properties. On the ther hand, De Jeu [17] suggested that birefringence can also be used to determine order parameter if a particular local field is applied to liquid crystals. on this basis, Kuczynski et al. [18] proposed a simple procedure, named Haller extrapolated approximation for estimation of order parameter from birefringence data. The birefringence, Δn, data as a function of temperature can be expressed as,

$$\Delta n = \Delta n_o \left(1 - \frac{T}{T^*}\right)^\beta \qquad (4)$$

where T* and β are two adjustable parameters, T* is (0-4)K higher than the clearing temperature and the critical exponent β depends on the molecular structure and its value is close to 0.2. Δn_0 is the extrapolated birefringence in the perfectly ordered state (i.e. at T= 0 K). The order parameter $<P_2>$ can be determined by the following equation

$$< P2 >= \frac{\Delta n}{\Delta n_o} \qquad (5)$$

The order parameter $<P_2>$ determined in this way describes well the nematic order parameter.

3.2. McMillan theory for smectic A phase

According to McMillan [15] the single particle potential for the smectic A phase is of the form,

$$\varepsilon(\cos\theta, z) = -\varepsilon_0\left[\delta\alpha\tau\cos(2\pi z/d) + \{\eta + \alpha\sigma\cos(2\pi z/d)\}P_2(\cos\theta)\right] \qquad (6)$$

Where the value of α and δ are adjustable parameters for the McMillan potential. d is the layer thickness, z is the displacement along the layer normal, $\eta = <P_2(\cos\theta)>$, the orientational order parameter, while $\tau = <\cos(2\pi z/d)>$ is the translational order parameter and $\sigma = <P_2(\cos\theta)\cos(2\pi z/d)>$ is the mixed translational and orientational order

parameter. The parameter ε_0 is obtained from the nematic-isotropic phase transition temperature, assuming the simple mean field theory result (kT_{NI}/ε_0=0.22019). The values of η, τ and σ are calculated using the self-consistency relationships as a function of temperature for several values of α and δ. The best fitted theoretical curve which was done by changing the α and δ value.

4. Results and Discussion

4.1. Orientational order parameter

The temperature dependence of order parameters ($<P_2>$) values obtained from optical birefringence measurement by optical transmission method are shown in the Figures 1(a)-(b). We determined the $<P_2>$ using the method described in section 3.1 employing Δn data measured in the entire mesomorphic phase. The extrapolated value of Δn_0 for compounds is nearly the same as Δn value measured from solid state. As obtained from Haller's extrapolation procedure, the extrapolated values of birefringence have been used to determine $<P_2>$ in both the nematic and smectic A phase. The fitting values of equation (4) are gathered in table 1. It is to be observed that the order parameter critical exponent value, β, lies between 0.149 and 0.153 which are quite well accordance with that predicted by theoretical values ($\beta<0.2$). The $<P_2>$ value in smectic A-isotropic (SmA-I) transition is increased with temperature due to long range order which decreases rapidly towards clearing temperature. Therefore, $<P_2>$ drops off progressively with increasing temperature until $<P_2>$ becomes zero.

Table 1. Parameter values of A, T (K) and β are obtained from Haller's fit at the nemetic to isotropic transition for (a) 11OCB, and (b) 12OCB

Compound	**A**	**T**	**β**
11OCB	0.361±0.071	360.20±0.076	0.153±0.029
12OCB	0.249±0.004	365.31±0.651	0.149±0.008

The experimentally obtained temperature dependence orientational order parameters (< P_2> values have been compared with the theoretical value determined by Maier and Saupe for compounds exhibiting smectic A phases.

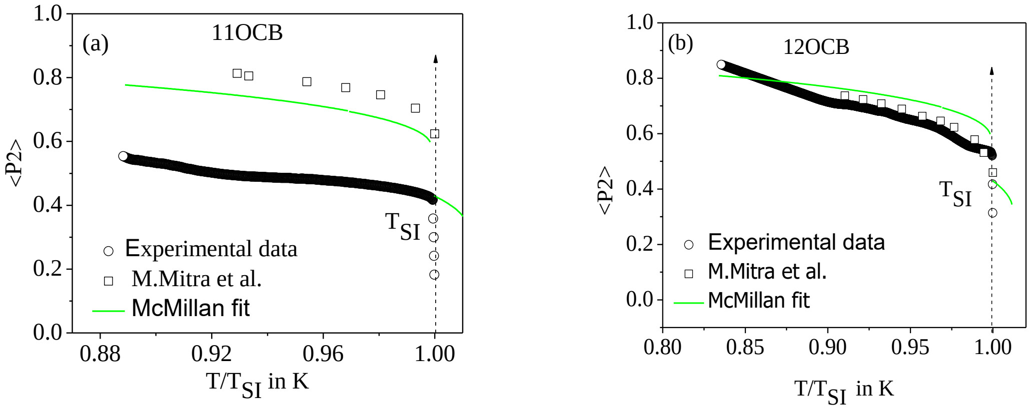


Figure 1. Variation of order parameter ($<P_2>$) with reduced temperature (T/T_{NI}) of compounds (a) 11OCB, and (b) 12OCB. O – Data Obtained from Optical Transmission Method with λ=632.8 nm. The Dashed Arrow Indicates the Nematic-Isotropic Transition Temperature (T_{NI})

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Table 2. Parameter values of α, δ and reduced temperature values for best fit with McMillan theory

Compounds	α	δ	T^*_{SN}	T^*_{NI}	T^*_{SI}
11OCB	0.536	0.5	-----	------	0.22019
12OCB	0.536	0.5	-----	-----	0.22019

5. Conclusions

A very simple and precise method, Haller's extrapolation method have been used for the determination of optical birefringence of undecyloxy-cyanobiphenyl (11OCB) and dodecyloxy-cyanobiphenyl (12OCB) crystalline. Using simple approximation, Haller's approximation, the Δn value can be used to calculate the order parameter, $<P_2>$. Haller's fit yields value very close to the predicted theoretically expected value, $\beta \sim 0.2$. The order parameter $<P_2>$ as a function of temperature has been derived from birefringence method shows in fairly good agreement with that obtained from Maier-Saupe theory for these compounds.

Declarations

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Competing Interests Statement

The author declares no competing financial, professional, or personal interests.

Consent for publication

The author declares that he consented to the publication of this study.

Authors' contributions

Author's independent contribution.

Availability of data and material

Supplementary information is available from the author upon reasonable request.

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